Highly Efficient Silicon-Based Anodes for Lithium-Ion Batteries

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Abstract. As the world shifts toward a more sustainable society, the advancement of high-performance lithium-ion battery (LIB) technology becomes increasingly vital in addressing rising CO_2 levels. The necessity for higher energy density, propelled by the progression of electric vehicles, hybrid electric vehicles, and portable electronics, has highlighted the limitations of traditional graphite anodes. Silicon-based anodes, with their superior theoretical capacity, present a promising alternative. This paper explores the working mechanisms of LIBs and delves into why silicon is an ideal material for anodes. It also delivers an exhaustive overview of Si-based electrodes, emphasizing the significant challenges they face, such as extreme volume expansion and unstable solid electrolyte interface (SEI) formation, which contribute to a shortened battery lifespan. Potential solutions, including nanostructured designs and novel binder formulations, are discussed, highlighting their advantages and current limitations. The benefits and challenges of Si-based materials as LIB anodes are summarized to guide future research and development in this critical area.

Keywords: Silicon-based anode; lithium-ion battery; electrode; electric vehicle.

1. Introduction

Traditional fossil fuel combustion will produce a lot of carbon dioxide and harmful gases such as nitrogen oxides and sulfides to aggravate the greenhouse effect and pollute the air. Moreover, Fossil fuels are limited resources, and because of our heavy dependence on them, they are expected to run out in the next few decades. Electric vehicles can be one of the most significant breakthroughs in reducing fossil fuel burning [1]. Rechargeable lithium-ion batteries (LIBs) are currently leading the energy storage market due to their high energy density and long lifespan, powering devices like smartphones and laptops, as well as electric vehicles. However, existing LIB technologies fall short of meeting the rapidly growing demands of electric vehicles, highlighting the urgent need for advancements in LIBs with ultrahigh energy and power density.

Silicon is an attractive candidate for next-generation LIBs due to its high natural abundance, environmental friendliness, relatively low lithiation potential, and impressive theoretical specific capacity of 4200 mAh/g [2]. However, silicon faces significant challenges in practical electrode applications, including substantial volume expansion (up to 300–400%) and difficulties in maintaining a stable solid electrolyte interface (SEI) [3]. A spectrum of challenges, including Silicon pulverization, structure degradation and significant thickness swelling, can be triggered by these phenomena [4].

Presently, the issues persist, but a variety of approaches have been implemented to mitigate these problems, as outlined briefly below. Silicon materials that incorporate nanotechnology, including nanoparticles and nanowires, have been employed in LIBs to prevent pulverization and shorten the lithium-ion diffusion pathway. Additionally, novel binders have been introduced to curtail volume fluctuations and to support the formation of a stable SEI.

This document provides an overview of recent advancements in the engineering of Si-based electrodes for high-energy-density applications. It begins by reviewing the fundamental principles of electrochemistry and identifying key challenges, such as the significant volume expansion and unstable SEI growth associated with silicon electrodes. The document then assesses current nanostructure design strategies aimed at addressing these issues, specifically focusing on methods to reduce volume expansion and stabilize the SEI. Next, it introduces innovative elastic binders with

high ionic conductivity as solutions to the mechanical stress caused by volume expansion. Finally, the document offers insights into the potential commercialization of Si-based anodes [2].

2. Reaction Mechanism of LIBs

A LIB is composed of a cathode made of lithium compounds, an anode of Si-based materials, an electrolyte, and a separator. Fig. 1 illustrates the basic working principle of a LIB.

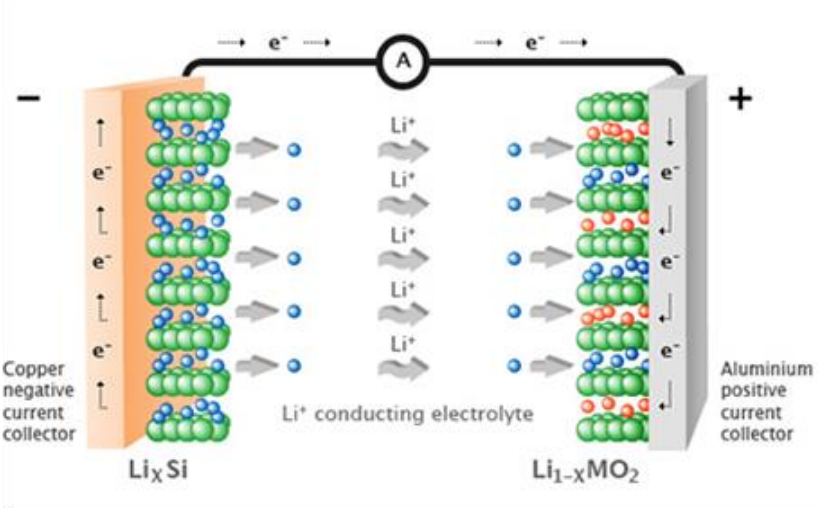


Fig. 1 Schematic diagram of the working mechanism of LIBs, reproduced from the website: https://www.cune.com.cn/news/hangye/3060.html

The battery operates by having lithium ions move between the positive and negative electrodes. During discharge, lithium ions are released from the negative electrode and embedded in the positive electrode via the electrolyte, causing the positive electrode to become lithium-rich. During charging, this process reverses.

Table 1. The performance comparison of graphite and Si-based electrodes

	Density (g/cm^3)	Theoretical specific capacity (mAh/g)	Li-insertion compound
Graphite	2.25	372	LiC_6
Silicon	2.33	4200	$Li_{15}Si_4$

The theoretical capacity of a LIB depends on the concentration of Li and the total number of electrochemical redox reactions available for energy storage. The comparations of performances of graphite and Si-based electrodes in several aspects (density, theoretical specific capacity and Li-insertion compound) are shown in Table 1 [5].

The theoretical specific capacity of Si is 4200 mAh/g. However, due to thermodynamic and kinetic constraints, each silicon atom can bond with 3 to 4 lithium ions to form $Li_{15}Si_4$, resulting in a practical capacity of 3579 mAh/g. In contrast, conventional materials like graphite require six carbon atoms to bond with just one Li-ion [6]. The microscopic molecular structure of $Li_{15}Si_4$ and LiC_6 are illustrated separately in Fig. 2 and Fig. 3.

The reaction mechanism is explained via the following equation: $Li_{15}Si_4$ (amorphous) ⇌ Si (crystalline) + x Li^+ + x e^- [7].

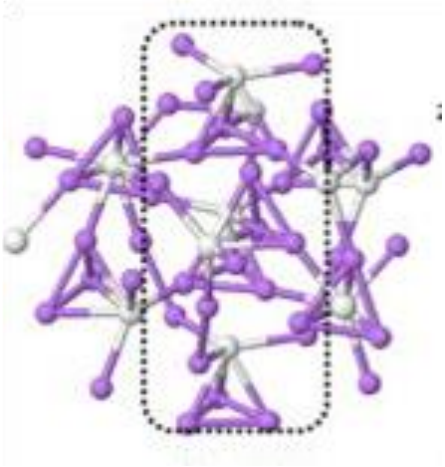


Fig. 2 Crystal structure of $Li_{15}Si_4$, with white spheres representing Si atoms and purple spheres representing Li atoms [6].

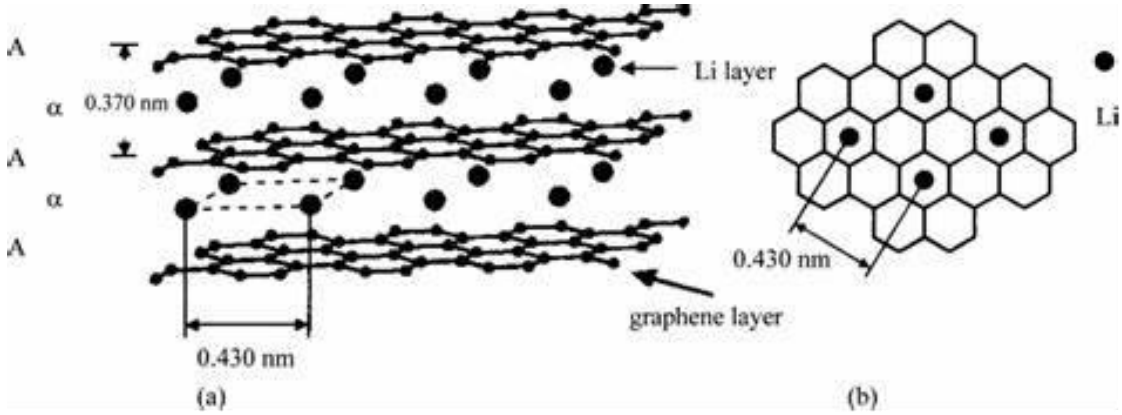


Fig. 3 Crystal structure for LiC_6, reproduced from the website: https://www.researchgate.net/post/

3. Detrimental Volume Expansion

The substantial difference in theoretical specific capacity between Si (4200 mAh/g) and graphite (372 mAh/g) stems from their ability to accommodate lithium ions. A single silicon atom can bond with 3 to 4 lithium ions ($Li_{15}Si_4$). However, in graphite, six carbon atoms are needed to accommodate one lithium ion (LiC_6). However, this high lithium-ion capacity in silicon leads to significant volume expansion—up to 300% to 400% when fully lithiated. This extensive expansion causes stability issues, with repeated lithium-ion insertion and extraction inducing mechanical stress, electrode cracking, and silicon pulverization, as illustrated in Fig. 4 and Fig. 5 [4].

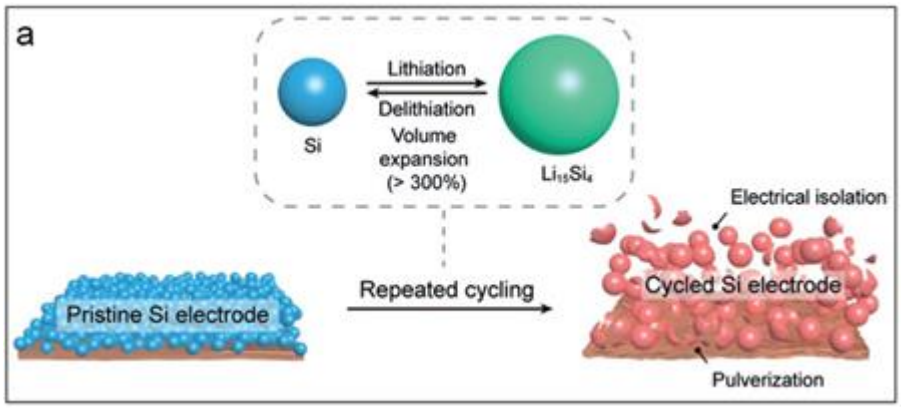


Fig. 4 Failure mechanisms of silicon electrodes include material pulverization, electrical isolation, and thickness expansion. Reproduced with permission [4].

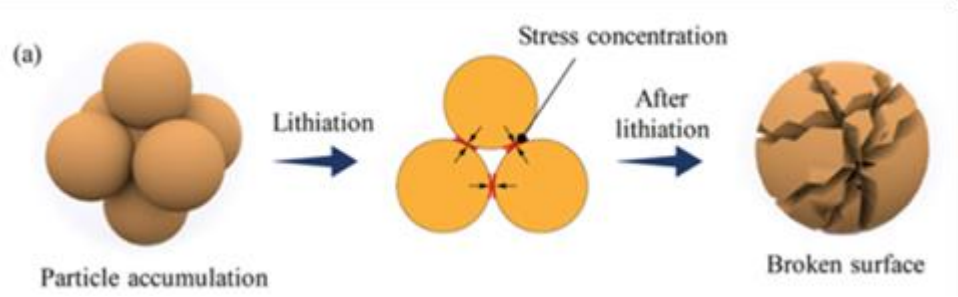


Fig. 5 The stress concentration and pulverization after volume expansion [4].

Ultimately, significant morphological changes due to volume alterations can lead to severe electrode expansion, which in turn causes the detachment of electrodes from their current collectors, resulting in a rapid decline in capacity.

4. Unstable SEI Growth

Beyond the challenges outlined earlier, significant volume alterations in Si anodes during cycling also catalyze the development of a detrimental SEI. When the anode's discharge potential falls below 1V, and the material becomes fully lithiated in the initial charge/discharge cycle, an SEI layer initiates its formation. This layer, composed of organic and inorganic compounds such as lithium alkyl carbonates ($ROCO_2Li$), Li_2O, Li_2CO_3, and LiF, results from the decomposition of the organic electrolyte. A well-formed SEI layer is advantageous as it acts as a protective barrier between the active materials and the electrolyte, preventing unwanted reactions. Simultaneously, it facilitates the efficient movement of Li-ions and serves as an electronic insulator, ensuring enhanced cycling stability.

Unfortunately, the cyclical volume fluctuations of Si during the Li insertion and extraction process can generate stresses that exceed what the fragile SEI can withstand, resulting in the undesirable and continuous growth of the SEI film, as Fig. 6 illustrates [8].

During volume expansion, the cracking of the SEI can expose fresh silicon to the electrolyte, resulting in continuous electrolyte consumption and longer lithium-ion diffusion paths. Additionally, the growth of the insulating SEI layer can weaken electrical contact between the Si-based materials and the current collector. This results in increased electrode impedance, reduced rate capabilities, and diminished cycling performance. Such persistent SEI growth is detrimental to the performance of LIBs.

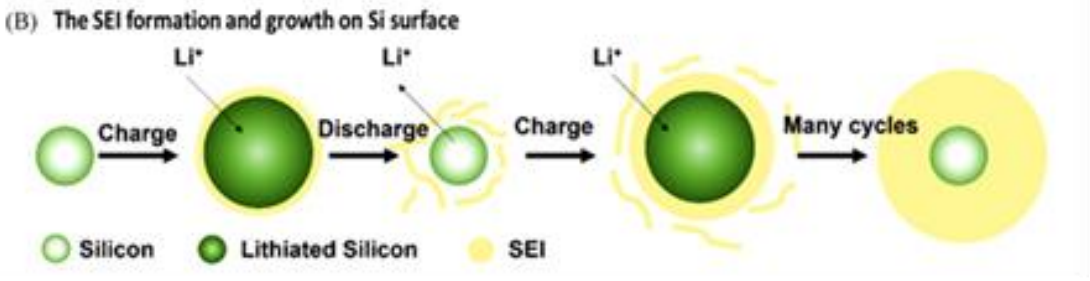


Fig. 6 Continuous SEI growth [9].

5. Strategic Design of Si-Based Electrodes

The strategic development of Si-based electrodes has been a subject of extensive research in recent years, aimed at mitigating the profound technical challenges inherent in their electrochemical properties. This review compiles nanostructural design approaches intended to reduce mechanical stress in high-capacity anodes, as well as cutting-edge binders and electrolyte additives that facilitate the stabilization of the SEI and enhance the kinetics of ion and electron diffusion.

5.1. 0D Silicon Nanoparticles

The manipulation of 0D nanoparticles has demonstrated that reducing the dimensions of Si electrode materials from the micrometer to the nanometer scale can enhance cycling performance and mitigate structural fracturing by alleviating internal strains. To clarify the direct relationship between particle size and the cycling stability of silicon anode materials, Huang and colleagues used in situ transmission electron microscopy to observe the morphology changes of silicon nanoparticles of different sizes during the initial lithiation process. It is depicted in Fig. 7 that nanoparticle with a diameter of 940 nm were reduced to a powdered state following the first lithiation, a phenomenon ascribed to the expansive mechanical tension encircling the silicon. Conversely, when the diameter decreased to 160 nm, Si nanoparticles exhibited substantial volume expansion without encountering fracturing or cracking [10].

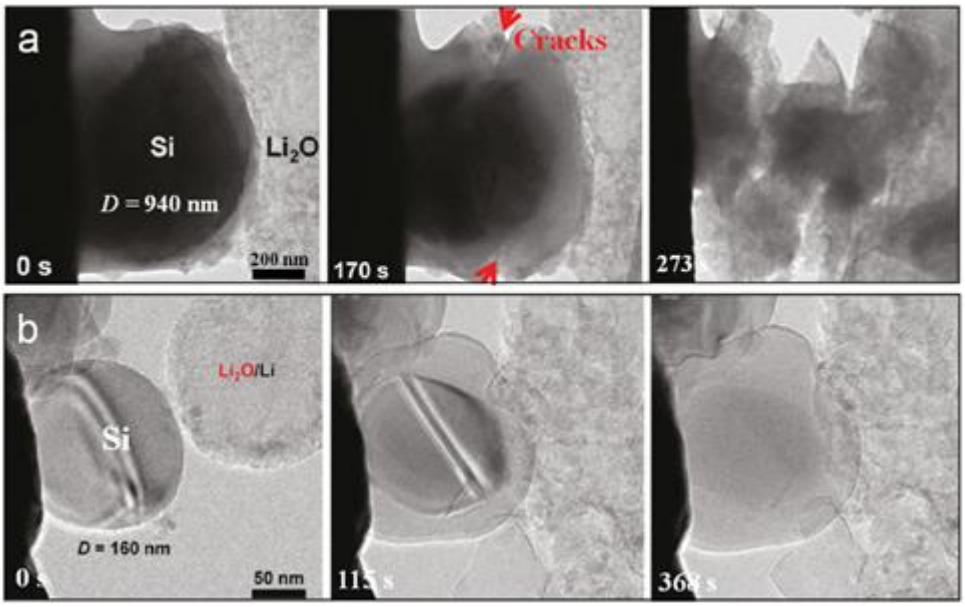


Fig. 7 In situ TEM images of (a) a large Si nanoparticle with a 940 nm diameter and (b) a small Si nanoparticle with a 160 nm diameter at different discharging states [10].

Nanostructured Si electrodes demonstrated shorter ionic and electronic diffusion paths and reduced mechanical stress from volume fluctuations when contrasted with bulk and micro-scale Si materials. These improvements collectively result in enhanced cycling stability and better rate performance [3].

5.2. 1D Silicon Nanostructures

However, utilizing 0D Silicon nanoparticles as anodes is not without some problems. The large specific surface area characteristic of nanoparticles might trigger significant parasitic reactions, depleting the electrolyte and compromising the battery's capacity [11].

1D Si structures, such as nanowires, nanotubes, and nanofibers, have been produced and exhibit potential as anode materials for LIBs in addition to 0D Si nanoparticles. Since the 1D nanostructured Si has a high aspect ratio, it efficiently inhibits pulverization by dispersing the mechanical strains from volume expansion radially and offers good paths for rapid Li-ion and electron diffusion along the axial direction [12].

A new type of Si–SiOx nanotube (DWSiNT) anode has been designed with double walls. Active silicon makes up the inside surface of DWSiNT, whereas limiting SiOx makes up the outer wall, which allows Li-ions to pass through. The electrolyte in this design cannot enter the inner hollow region; instead, it comes into touch with the outer surface. Li-ions pass through the outer wall during lithiation and interact with the inner silicon wall. Because of the mechanical strength of the outer wall, the inner silicon wall expands inward into the hollow space. This inward expansion is made feasible by the significant softening of silicon that occurs when lithium is inserted. The silicon wall's inner

surface retracts during delithiation. Generally, during the lithiation and delithiation processes, the interface with the electrolyte is subjected to mechanical restraint and remains in a static condition. The inner surface is the only part that moves without making contact with the electrolyte. Two attractive properties of the DWSiNT structure as an anode material are as follows: (1) A stable SEI layer is encouraged to form by the immobile outer surface. (2) Without mechanical breakage, the interior space allows Si to expand its volume without restriction [13].

6. Novel Binder Design

In LIBs, the binder is crucial for maintaining the stability of the electrodes during repeated expansion and contraction cycles. It helps prevent the active particles from loosening or degrading, and it stops them from separating from the current collector.

Binders are generally classified into two types: NMP-soluble and water-soluble. NMP-soluble binders are part of the traditional system, often used with polyvinylidene difluoride (PVDF). Water-soluble binders, on the other hand, are a recent development aimed at replacing the toxic and expensive NMP with more eco-friendly and cost-effective water. Research suggests that water-soluble binders may offer better electrochemical performance compared to the NMP-PVDF systems. Previous research has demonstrated that water-soluble binders outperform NMP-PVDF-based systems in terms of electrochemical performance. Studies have explored the impact of water-soluble binders, such as carboxymethyl cellulose (CMC) and sodium alginate (SA), on high-voltage lithium nickel manganese oxide (LNMO) cathodes, revealing that LNMO cathodes made with these aqueous binders exhibit superior cycling stability.

Additionally, a novel water-soluble bifunctional binder has been developed by combining a conductive polythiophene polymer (PED) with the highly adhesive PAA. This new binder has shown outstanding performance in Si-based anodes, including high reversible capacity, excellent cycle stability, and impressive high-rate capacity. Experiments using a water-soluble polyamide acid (WS-PAA) binder with ionic bonds have provided satisfactory mechanical strength for SiO_x anodes, resulting in improved cycling performance and rate capability. Furthermore, a water-soluble PAAS–CDP–PAA binder with enhanced adhesion, lithium diffusion, and structural integrity has led to increased specific capacity and capacity retention for Si electrodes [14].

7. Conclusion

In conclusion, Si-based materials hold significant promise as anodes for next-generation LIBs due to their high theoretical specific capacity, affordability, and favorable redox potential. However, two major challenges hinder their widespread adoption: volume expansion during charging and unstable SEI growth. Despite advancements, Si and Si-based electrodes remain underdeveloped for large-scale practical use. This paper addresses the primary challenges and recent innovations in designing Si-based electrodes for practical applications, focusing on fundamental electrochemistry and critical issues. The challenges include substantial volume expansion and unstable SEI growth, which contribute to shorter battery life. Novel engineering solutions, such as nanostructured designs and advanced binders, have been developed to address these issues. Reducing particle sizes to the nanoscale can help manage volume changes, minimize pulverization, shorten Li-ion diffusion paths, and improve reaction kinetics. New binders have also been introduced to mitigate volume fluctuations and stabilize SEI formation.

The ongoing challenge in LIB technologies is balancing high performance with cycling stability, as current solutions fail to meet the growing demand for higher energy densities. Commercially available Si-containing LIBs usually have a low Si content, typically less than 10 wt.%. An enhancement in the Si content ratio could potentially elevate energy density significantly. However, such an increase would likely compromise cycling stability and give rise to safety concerns. Thus, if

a comprehensive understanding of their optimal functionality, Si-based batteries with high energy density could be of great importance for helping the world switch to a time after using fossil fuels.

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